

Stability and oxygen permeation behavior of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}\text{-La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ composite membrane under large oxygen partial pressure gradients

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Abstract

The stability and oxygen permeation behavior of the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}\text{-La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ dual-phase composite were investigated under a large oxygen gradient with one side of it exposed to air and the other side to CO, CH₄ or H₂ at elevated temperatures. An oxygen permeation flux of $8.6 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ was obtained with a 1.1 mm thick membrane tube under air/CO gradient at 950 °C, and no decrease in the flux was observed within a period of 110 h. The oxygen flux under air/CO gradient was found to be about twice that under air/CH₄ or air/H₂ gradients, which may be attributed to the higher catalytic activity of the membrane towards the oxidation of CO. The membrane tube remained intact after high temperature operation for over 1000 h, and no significant change in the phase composition and microstructure occurred. The dual-phase composite may satisfy the stability requirement under the stringent membrane reactor conditions.

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1. Introduction

The dense ceramic membrane made of mixed oxygen ion and electron conducting oxides has received increasing attention for their potential applications in upgrading of the natural gas through the partial oxidation of methane (POM) [1–4]. For successful applications, the membrane is required to possess both high oxygen permeability and sufficient stability under an oxygen partial pressure gradient at high temperatures. In the POM membrane reactor, the membrane must withstand oxidizing atmosphere (air) on one side of it and highly reducing atmosphere (methane) with oxygen partial pressure down to $\sim 10^{-19}$ bar on the other side at high temperatures [3]. Currently, most of membrane materials investigated are single-phase perovskite oxide $(\text{Ln}, \text{A})(\text{Co}, \text{Fe}, \text{B})\text{O}_{3-\delta}$ (Ln = rare earth elements, A = Ca, Sr, Ba, B = transition metal elements or Ga) [1–8]. These oxides

possess high oxygen permeability [4–7], but have problems in long-term durability under POM reactor conditions [3,7,8]; Fe-doped LaGaO₃ may be an exception, which has been reported to be able to satisfy both requirement on the permeability and stability, but the use of costly Ga element may limit its practical applications [4]. A possible way round the stability problems facing the single-phase membrane is adoption of dual-phase composite, in which oxygen ions transport through one phase while electrons through the other phase [9–11].

In the previous paper [12], it has been shown that the composite membrane consisting of oxygen ion conductor $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ (denoted SDC) (60 vol.%) and electron conductor $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ (denoted LSC) exhibits appreciable oxygen permeability under a small differential oxygen pressure (air/helium) at elevated temperatures, and no observable reactions between the two constituent oxides occur during high temperature sintering and permeation measurements. It has also been shown that the SDC and LSC oxides, which function respectively as oxygen ion conducting membrane and interconnect in solid oxide fuel cells (SOFCs), can maintain their

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integrity in both oxidizing and reducing atmospheres at elevated temperatures [13,14]. Therefore, the composite of these two oxides are expected to remain stable under the stringent chemical reactor conditions. This paper is to report the stability and the oxygen permeation properties of SDC-LSC composite under a large oxygen gradient at elevated temperatures with one side of it exposed to the ambient air and the other side to CO, CH₄ or H₂.

2. Experimental

Details on sample preparation are given in Ref. [12]. Fluorite Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) powder was obtained by oxalate complexation-precipitation and perovskite La_{0.8}Sr_{0.2}CrO_{3-δ} (LSC) powder was synthesized via a conventional solid-state reaction route. The SDC and LSC powders were mixed in a mortar at a weight ratio of 63:37 (volume ratio 60:40) and carefully ground, cold isostatically pressed into tubes or pellets under a pressure of 300 MPa, and then subjected to sintering at 1550 °C for 10 h in air. The density of the sintered sample was measured to be of 88–90% of the theoretical density using Archimedes method in mercury. The phase composition of the ceramics was analyzed by X-ray diffraction (XRD) (Philips X'Pert Pro Super, Cu Kα), and its microstructure examined with scanning electron microscopy (SEM) (JEOL JSM-6700F). The fresh sintered sample was found to consist of SDC and LSC phase.

Prior to oxygen permeation measurements, the sintered membrane tube was polished at its outer wall, and ultrasonically cleaned in ethanol. A membrane tube of length 30.5 mm, outer diameter 8.9 mm and wall thickness 1.1 mm was sealed with glass rings between two alumina tubes at 1000 °C in stagnant air. After sealing, the outer wall of the membrane tube was exposed to the ambient air, while CO, CH₄ or H₂ was fed into the tube at fixed rate of 30 ml min⁻¹ to react with oxygen permeated from the air side. The gas composition in the effluent was analyzed by gas chromatographs (SHIMADZU 14C and GC9750), and the oxygen permeation rate was determined [15]. Note that the oxygen leaked from the air due to the partial failure of glass sealing and imperfection present in the membrane tube was corrected, which amounted to less than 2% of the permeated oxygen.

3. Results and discussion

Fig. 1 shows the temperature dependence of oxygen permeation fluxes (J_{O_2}) through a 1.1 mm thick SDC-LSC membrane tube when one side of it was exposed to air (feed side) and the other to CO, H₂ or CH₄ (permeate side). (Note that the oxygen flux was measured after attaining a steady state.) The steady oxygen flux increases with increasing temperature as expected. At 950 °C, an oxygen permeation flux was measured to be 8.6×10^{-7} mol cm⁻² s⁻¹ under air/CO gradient; in this case, the oxygen partial pressure inside the membrane tube was estimated to be 1.2×10^{-15} bar. Due to the much larger oxygen gradient imposed to the membrane, the resulting oxygen permeation flux is one order of magnitude higher than that under a small oxygen gradient (air/He) for a disk-shaped SDC-LSC membrane of the same thickness [12]. The oxygen permeation

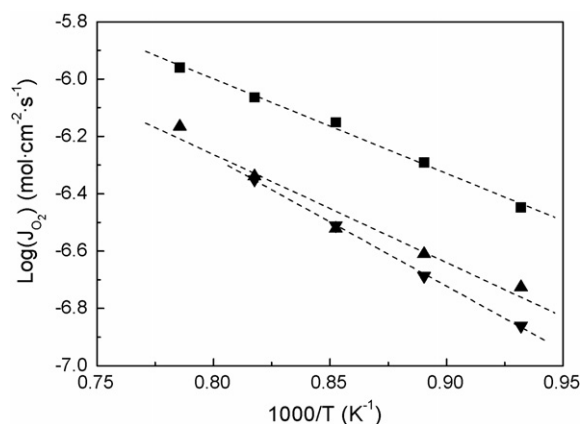


Fig. 1. Arrhenius plots of oxygen permeation fluxes through a 1.1 mm thick membrane tube by exposing one side of it to air and the other side to (■) CO, (▲) H₂, (▼) CH₄. Dashed lines are guides to the eye.

flux is much lower when CH₄ or H₂ is fed into the membrane tube. A flux of 2.1×10^{-7} mol cm⁻² s⁻¹ was observed at 850 °C at a CH₄ feed rate of 30 ml min⁻¹, which is comparable to that of a SrFeCo_{0.5}O_x membrane at a CH₄ feed rate of 2 ml min⁻¹ [1]. The apparent activation energy for oxygen permeation is found to decrease in the order of CO < H₂ < CH₄ in the range from 63 to 86 kJ mol⁻¹. Since the (equilibrium) oxygen partial pressures in CO, H₂ and CH₄-containing atmospheres are estimated not to differ much under the given conditions, the difference in the oxygen permeation behavior certainly reflects the difference in the catalytic activity of the membrane surface towards the oxidation reactions of these reducing species. In fact, it has been reported by Doshi et al. that when La_{0.8}Sr_{0.2}CrO_{3-δ} was used as a catalyst for CO or CH₄ oxidation, a conversion of 50% was attained at 136 °C for CO while only 5% of CH₄ was oxidized at a much higher temperature of 700 °C [16]. It has also been reported that doping of Ni or Mn in LSC can greatly improve its catalytic properties for the oxidation of CH₄ and H₂ [17,18]. It is likely that the oxygen permeability of the composite membrane can be further improved by doping the LSC phase with appropriate amounts of Ni and Mn.

In order to investigate the performance stability of the composite membrane, the membrane tube was also tested under air/CO gradient for a period of 110 h at 950 °C, and the time dependence of the flux is shown in Fig. 2. It can be seen that the oxygen flux varies slightly in the range of $(8.3\text{--}9.0) \times 10^{-7}$ mol cm⁻² s⁻¹, suggesting no degradation of the membrane in the course. It was reported by Kharton et al. that the oxygen permeation flux of Ce_{0.8}Gd_{0.2}O_{2-δ}-La_{0.7}Sr_{0.3}MnO_{3-δ} composite membrane started to decrease after operation for about 70–100 h at 950 °C under an air/He gradient, which was attributed to the reaction of the two constituent phases [19]. Compared with LaMnO₃, LaCrO₃ possesses a larger crystal-field stabilization energy value and is more thermodynamically stable towards yttria-stabilized zirconia [20]. Therefore, it is likely that La_{0.8}Sr_{0.2}CrO_{3-δ} is more stable than La_{0.7}Sr_{0.3}MnO_{3-δ}, and less reactive towards ceria. This may account for the stable oxygen permeation performance of the resulting SDC-LSC composite membranes as shown in Fig. 2.

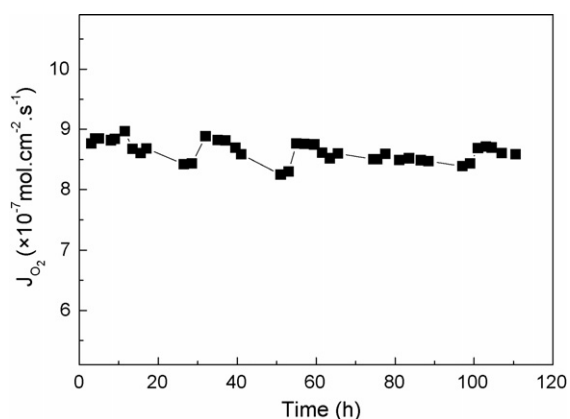


Fig. 2. Time dependence of oxygen permeation flux at 950 °C under air/CO gradient.

The membrane tube used in the above-described measurements was also used to study the influences of feed composition and flow rate on the oxygen permeation flux at constant temperature of 950 °C. (For the sake of simplicity, the data is not given in the present paper.) The membrane tube underwent ~ 1000 h of oxygen permeation measurements under various conditions, but still remained intact. SEM analysis reveals that in comparison with the membrane tube before oxygen permeation measurement [12], its microstructure was largely retained at the feed

side (Fig. 3a and b); the surface at the permeate side, however, became porous and rough after high temperature operation, and these changes are found to be limited to the outermost surface layer (Fig. 3c and d). Close examination shows that pores appear in the SDC grains at the permeate side, but not in the LSC grains (Fig. 3d). The occurrence of the pores is likely related to the valence change of the cerium ions in SDC phase under the reducing atmosphere. It has been reported that reduction of Ce^{4+} to Ce^{3+} in $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ led to micro-cracks due to the associated volume expansion and consequently a drastic decrease in the ionic conductivity [21]. However, in the present study, the composite membrane was operated under the critical environments for over 1000 h without occurrence of leakage, and no micro-cracks were observed by SEM on the used membrane. Probably, the mechanical integrity of the ceria is improved through making composite with LSC, as the latter is known to possess excellent stability in reducing atmosphere [17,22]. The ceria used in the present study is doped with Sm, which may also have a better stability in comparison with ceria doped with Gd [23].

To examine the possible change in phase composition during the high temperature operation of the membrane, a polished pellet was also subjected to an oxygen permeation measurement under an air/(60 vol.% H_2 + Ar) gradient for a period of 72 h and was examined by XRD. It is revealed that SDC and LSC remain as main phases at the surfaces of both the feed and permeate

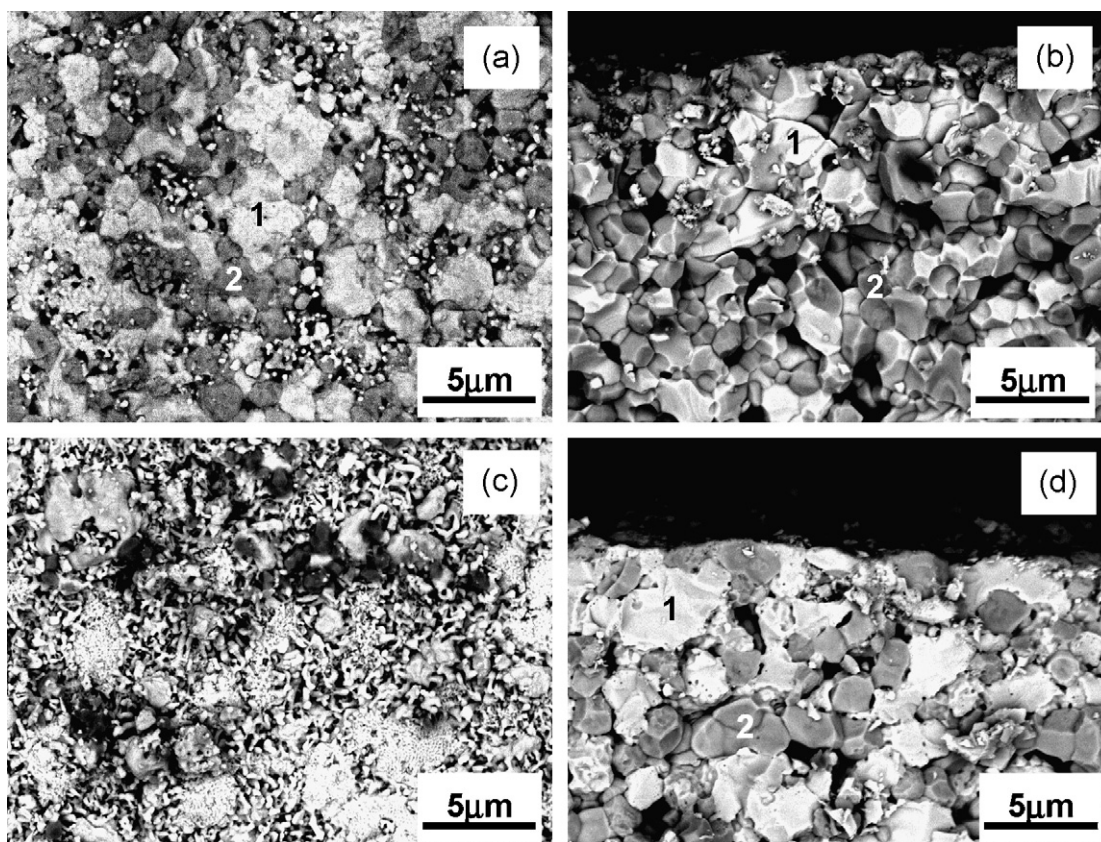


Fig. 3. Backscattered electron images of the membrane tube after oxygen permeation measurements. (a) Top view for the feed side surface, (b) fractured view near the feed side, (c) top view for the permeate side surface and (d) fractured view near the permeate side. The numbers 1 and 2 in (a) denotes $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_{3-\delta}$ phase, respectively, and the black holes in the pictures correspond to pores in the samples.

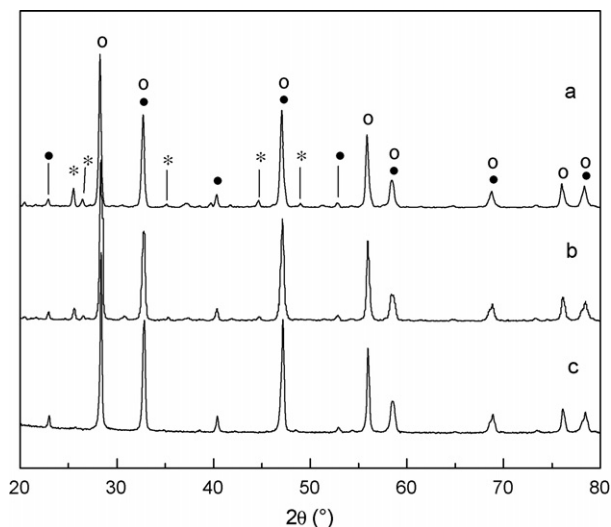


Fig. 4. XRD patterns for a composite pellet after permeation under air/(60 vol.% H₂ + Ar) gradient. (a) Feed side, (b) permeate side and (c) polished surface (bulk). (○) Ce_{0.8}Sm_{0.2}O_{2-δ}, (●) La_{0.8}Sr_{0.2}CrO_{3-δ}, (*) unknown phase.

side (Fig. 4a and b). Some extra weak peaks appear, indicating the formation of impurity phase; further analysis shows that this impurity phase exist only in the surface layer, as the weak peaks were no longer observed for the used membrane after slight polishing (Fig. 4c). Similar observation was found for the disk-shaped SDC-LSC membrane subjected to oxygen permeation under an air/He gradient, where the formation of such impurity phase was attributed to volatilization of Cr species in LSC at high temperatures [12]. Apparently, the oxygen permeability of the composite is not adversely affected by its occurrence on the membrane surface under the given experimental conditions (Fig. 2).

4. Conclusion

The Ce_{0.8}Sm_{0.2}O_{2-δ}–La_{0.8}Sr_{0.2}CrO_{3-δ} dual-phase membrane exhibits appreciable and stable oxygen permeability at elevated temperatures under large oxygen gradients with one side exposed to air and the other side to CO, CH₄ or H₂. And the membrane tube can retain its mechanical integrity, and preserve its microstructure and phase composition to a large degree, under such stringent conditions.

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